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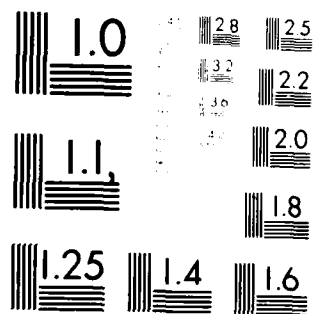
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Ionic Conductivity in Lithium Hexaoxometallate

Solid Solutions

By

E. Nomura and M. Greenblatt

Prepared for Publication

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# IONIC CONDUCTIVITY IN LITHIUM HEXAOXOMETALLATE SOLID SOLUTIONS

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A

## ABSTRACT

Lithium ion conductivity in solid solutions formed between  $\text{Li}_7\text{TaO}_6$ ,  $\text{Li}_7\text{M}^{\text{V}}\text{O}_6$  ( $\text{M}^{\text{V}} = \text{Nb, Bi}$ ) and  $\text{Li}_8\text{ZrO}_6$  has been measured as a function of temperature and composition using complex impedance method. The samples prepared were  $\text{Li}_7\text{Ta}_{1-x}\text{Nb}_x\text{O}_6$ ,  $\text{Li}_7\text{Ta}_{1-x}\text{Bi}_x\text{O}_6$  and  $\text{Li}_{7+x}\text{Ta}_{1-x}\text{Zr}_x\text{O}_6$ . At  $200^\circ\text{C}$ , the conductivities of  $\text{Li}_7\text{Ta}_{0.7}\text{Nb}_{0.3}\text{O}_6$ ,  $\text{Li}_7\text{Ta}_{0.6}\text{Bi}_{0.4}\text{O}_6$  and  $\text{Li}_{7.4}\text{Ta}_{0.6}\text{Zr}_{0.4}\text{O}_6$  are  $4.3 \times 10^{-4} (\Omega\text{cm})^{-1}$ ,  $3.0 \times 10^{-4} (\Omega\text{cm})^{-1}$  and  $4.0 \times 10^{-4} (\Omega\text{cm})^{-1}$ , respectively.

## INTRODUCTION

There is considerable interest in developing solid lithium ion conductors for utilization in high energy density battery systems. This has led to a search for new solid electrolytes exhibiting high lithium ion conductivity and has stimulated interest in developing a fundamental understanding of ionic transport in solids<sup>(1-3)</sup>.

The compounds of lithium hexaoxometallates, formulated as  $\text{Li}_n\text{MO}_6$ ;  $n = 6, 7$  or  $8$ ,  $\text{M} = \text{IV, V or VI group element}$ , have a pseudo two dimensional structure and high lithium ion conductivity<sup>(4)</sup>. The structure of  $\text{Li}_n\text{MO}_6$  is characterized by octahedral sheets of  $\text{CdI}_2$ -type, between which  $6 \text{ Li}^+$  are inserted in a tetrahedral environment as



$$a+b+c = 3$$

□: vacancy

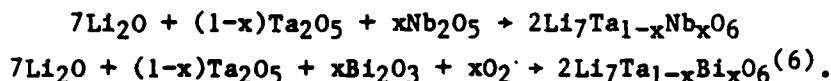
Among the lithium hexaoxometallates,  $\text{Li}_7\text{TaO}_6$  (i.e.  $\text{Li}_6(\text{LiTa}\square)\text{O}_6$ ) is the best lithium conductor with  $\sigma_{200} = 5 \times 10^{-4} (\Omega\text{cm})^{-1}$  and  $\sigma_{\text{RT}} = 4.3 \times 10^{-8} (\Omega\text{cm})^{-1}$ (4).

It has been shown that the activation energy for  $\text{Li}^+$  diffusion in the tetrahedral sites between the layers is significantly larger than that for the octahedral lithium ion in the layers<sup>(5)</sup>. Thus by altering the lithium content and/or the vacant sites in the layers higher ionic conductivities might be achieved. We have examined the effect of increased  $\text{Li}^+$  content by partial substitution of tantalum ions with  $\text{Zr}^{4+}$  to yield  $\text{Li}_6(\text{Li}_{1+x}\text{Ta}_{1-x}\text{Zr}_x \square_{1-x})\text{O}_6$ . We have also attempted to look at the effect of decreased  $\text{Li}^+$  content (or increased vacancies) in the layers by studying the conductivities of samples with substituted divalent cations (e.g.  $\text{Li}_6(\text{Li}_{1-2x}\text{Mg}_x\text{Ta} \square_{1+x})\text{O}_6$ ), however our results are inconclusive on this system due to difficulties in obtaining single phase compounds.

Alternatively we hoped to obtain higher lithium conductivities in this system by partial substitution of the tantalum ions with other group V metal ions of larger ionic radii in order to optimize the channel size of the framework structure for lithium diffusion. In this paper we report the results of the lithium conductivity in:  $\text{Li}_7\text{Ta}_{1-x}\text{Nb}_x\text{O}_6$ ,  $\text{Li}_7\text{Ta}_{1-x}\text{Bi}_x\text{O}_6$ ,  $\text{Li}_{7+x}\text{Ta}_{1-x}\text{Zr}_x\text{O}_6$ .

### EXPERIMENTAL

$\text{Li}_2\text{O}$  was obtained by thermal decomposition of anhydrous  $\text{Li}_2\text{O}_2$  in vacuum at  $450^\circ\text{C}$  for 6 hours. Other starting materials were reagent grade  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{ZrO}_2$ . Mixtures of appropriate composition were thoroughly mixed using agate mortar in a He dry box. For example,  $\text{Li}_7\text{Ta}_{1-x}\text{Nb}_x\text{O}_6$  and  $\text{Li}_7\text{Ta}_{1-x}\text{Bi}_x\text{O}_6$  were prepared from  $\text{Li}_2\text{O}$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$ , and  $\text{Li}_2\text{O}$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Bi}_2\text{O}_3$ , respectively, according to the following equation



The mixtures were pressed into cylindrical pellets  $3/8$ " diameter and about 0.2" thick at 15 kpsi. The pressed pellets were transferred to high purity alumina crucibles, were embedded in excess  $\text{Li}_2\text{O}$  powder in order to prevent  $\text{Li}_2\text{O}$  losses, and were heated at  $650^\circ\text{C}$  for 18 hours in air. After cooling, the pellets were crushed and examined by X-ray powder diffraction using a Norelco diffractometer with Ni filtered copper radiation. Lithium content was determined by atomic absorption spectrophotometric methods.

Pellet samples for ionic conductivity measurements were prepared by pressing to  $1/4$ " diameter and about 0.15" thickness at 30 kpsi followed by sintering at  $950^\circ\text{C}$  for 18 hours in air and quenching in air. Again,  $\text{Li}_2\text{O}$  loss was minimized by covering the pellets with  $\text{Li}_2\text{O}$  powder during the sintering process. The X-ray diffraction pattern and lithium content of the sintered samples were checked to confirm the identity and composition of the phases present. Weight loss was not observed after sintering. The density of the sintered pellets were about 85% of theoretical value. Both surfaces of the pellets were polished using silicon carbide (#400) paper and sputtered with about  $1\mu\text{m}$  of gold followed by a coating of silver paint (Engelhard #16).

The device for the conductivity measurement is shown in Fig. 1. Platinum contact leads were made by spot welding pieces of platinum foil of  $10 \times 10 \text{ mm}^2$  to platinum wires. Two discs of  $\alpha$ -alumina of 10 mm diameter and 3 mm thickness were used for insulating the materials. Contact between the sample electrode (sputtered gold and painted silver) and the platinum lead was made

Fig. 1  
Device for conductivity measurement

- |                           |                         |
|---------------------------|-------------------------|
| 1. sample Pellet          | 3. platinum lead        |
| 2. $\alpha$ -alumina disc | 4. stainless steel disc |
| 5. screw                  |                         |

Fig. 2  
Circuit diagram for AC conductivity measurement

- |                         |  |
|-------------------------|--|
| A. tuned amplifier      | PS. phase shifter                      |
| M. mixer                | I. integrator                          |
| R <sub>x</sub> . sample | R <sub>std</sub> . standard resistance |

by tightening the screw (Fig. 1). The AC conductivity measurements were made using ionically blocking electrodes. The schematic electrical circuit diagram of the AC conductivity measurement is shown in Fig. 2. Lock-in amplifier (PAR Model 128A) was used as a phase sensitive detector and a Hewlett-Packard Model 200 CDR was used as a signal generator. The frequency range used was between 5 HZ and 100 KHZ. The measurement temperature was from room temperature to 250°C in air.

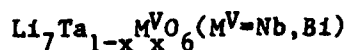
## RESULTS AND DISCUSSIONS

### Li<sub>7</sub>TaO<sub>6</sub> ~~~~~

The ionic conductivity of  $\sigma_{200} \approx 5 \times 10^{-4} (\Omega \text{ cm})^{-1}$  and activation energy of 0.66 eV of Li<sub>7</sub>TaO<sub>6</sub> have been measured by C. Delmas et al<sup>(4)</sup>. We have also measured the conductivity of sintered pellets of Li<sub>7</sub>TaO<sub>6</sub>. Fig. 3 shows the conductivity,  $\sigma$  versus  $1/T$  of Li<sub>7</sub>TaO<sub>6</sub>. Different activation energies corresponding to a lower and higher temperature regions are observed. In the higher temperature region, the deviation of ionic conductivity between different pellets is small (which is also a measure of the reliability of the data) and the activation energy is 0.67 eV. In the lower temperature region, the ionic conductivity of different pellets differ more significantly but the activation energies are the same (0.46 eV). The change in the slope of the  $\sigma$  vs  $1/T$  plot of Li<sub>7</sub>TaO<sub>6</sub> probably corresponds to a transition from extrinsic to intrinsic conductivity regions; then the variations in the ionic conductivities of different samples in the lower temperature region can be explained by differences in defect concentrations or particle packing from sample to sample.

Fig. 3

The temperature dependence of  
the conductivity of Li<sub>7</sub>TaO<sub>6</sub>



The X-ray diffraction patterns of the solid solutions prepared were identical to that of  $\text{Li}_7\text{TaO}_6$  except for the shifts in  $2\theta$ . The lattice parameters calculated for a hexagonal unit cell increased with increasing values of  $x$  for  $\text{Li}_7\text{Ta}_{1-x}\text{Nb}_x\text{O}_6$  and for  $\text{Li}_7\text{Ta}_{1-x}\text{Bi}_x\text{O}_6$ ;  $a = 5.42\text{\AA}$ ,  $c = 15.17\text{\AA}$  for  $\text{Li}_7\text{Ta}_{0.6}\text{Nb}_{0.4}\text{O}_6$  and  $a = 5.44\text{\AA}$ ,  $c = 15.23\text{\AA}$  for  $\text{Li}_7\text{Ta}_{0.6}\text{Bi}_{0.4}\text{O}_6$ . The lattice parameters of  $\text{Li}_7\text{TaO}_6$ ,  $\text{Li}_7\text{NbO}_6$  and  $\text{Li}_7\text{BiO}_6$  are  $a = 5.39\text{\AA}$ ;  $c = 15.11\text{\AA}$ ;  $a = 5.40\text{\AA}$ ;  $c = 15.12\text{\AA}$ ; and  $a = 5.50\text{\AA}$ ,  $c = 15.45\text{\AA}$ , respectively<sup>(7)</sup>. It is clear that the lattice parameters of  $\text{Li}_7\text{Ta}_{0.6}\text{Nb}_{0.4}\text{O}_6$  are larger than those of either of the component compounds,  $\text{Li}_7\text{TaO}_6$  and  $\text{Li}_7\text{NbO}_6$ , while the lattice parameters of  $\text{Li}_7\text{Ta}_{0.6}\text{Bi}_{0.4}\text{O}_6$  are intermediate between those of  $\text{Li}_7\text{TaO}_6$  and  $\text{Li}_7\text{BiO}_6$ . The variation of lattice parameters with  $x$  in  $\text{Li}_7\text{Ta}_{1-x}\text{Nb}_x\text{O}_6$  and  $\text{Li}_7\text{Ta}_{1-x}\text{Bi}_x\text{O}_6$  is shown in Fig. 4. The bismuth substituted phases appear to obey Vagard's law while the  $\text{Li}_7\text{Ta}_{1-x}\text{Nb}_x\text{O}_6$  system does not. This suggests that there might be a new phase close to the  $\text{Li}_7\text{Ta}_{0.6}\text{Nb}_{0.4}\text{O}_6$  composition.

The ionic conductivities of  $\text{Li}_7\text{Ta}_{1-x}\text{Nb}_x\text{O}_6$  are shown in Fig. 5. The ionic conductivities increase from  $1.1 \times 10^{-4} (\Omega \text{ cm})^{-1}$  for  $x = 0.0$  to  $4.3 \times 10^{-4} (\Omega \text{ cm})^{-1}$  for  $x = 0.3$  at  $200^\circ\text{C}$  and decrease as  $x$  is increased further (Fig. 5). The activation energy of conduction is  $0.63 \text{ eV}$  for  $\text{Li}_7\text{Ta}_{0.7}\text{Nb}_{0.3}\text{O}_6$ , somewhat smaller than the  $0.67 \text{ eV}$  observed for  $\text{Li}_7\text{TaO}_6$ .

The ionic conductivities of  $\text{Li}_7\text{Ta}_{1-x}\text{Bi}_x\text{O}_6$  phases are shown in Fig. 6. The ionic conductivities increase to  $3.0 \times 10^{-4} (\Omega \text{ cm})^{-1}$  at  $200^\circ\text{C}$  at  $x = 0.4$ . The activation energy for conduction is  $0.60 \text{ eV}$  in  $\text{Li}_7\text{Ta}_{0.7}\text{Bi}_{0.3}\text{O}_6$ .

Fig. 4  
Lattice parameters of  
 $\text{Li}_7\text{Ta}_{1-x}\text{Nb}_x\text{O}_6(0)$  and  
 $\text{Li}_7\text{Ta}_{1-x}\text{Bi}_x\text{O}_6(0)$

Fig. 5  
The temperature dependence of the  
conductivity of  $\text{Li}_7\text{Ta}_{1-x}\text{Nb}_x\text{O}_6$   
phases

Fig. 6  
The temperature dependence of the  
conductivity of  $\text{Li}_7\text{Ta}_{1-x}\text{Bi}_x\text{O}_6$   
phases

In the  $\text{Li}_7\text{Ta}_{1-x}\text{Nb}_x\text{O}_6$  and  $\text{Li}_7\text{Ta}_{1-x}\text{Bi}_x\text{O}_6$  phases the observed increase in ionic conductivity and decrease in activation energy at  $x = 0.3$  and  $0.4$  respectively compared to  $\text{Li}_7\text{TaO}_6$  is clearly due to optimizing the channel size for lithium diffusion at these compositions.

#### $\text{Li}_{7+x}\text{Ta}_{1-x}\text{Zr}_x\text{O}_6$

The powder X-ray diffraction pattern of  $\text{Li}_{7+x}\text{Ta}_{1-x}\text{Zr}_x\text{O}_6$  is similar to that of  $\text{Li}_7\text{TaO}_6$ . The lattice parameters increased with increasing values of  $x$ ;  $a = 5.44\text{\AA}$  and  $c = 15.25\text{\AA}$  were found for  $\text{Li}_{7.4}\text{Ta}_{0.6}\text{Zr}_{0.4}\text{O}_6$ .

The ionic conductivities of  $\text{Li}_{7+x}\text{Ta}_{1-x}\text{Zr}_x\text{O}_6$  are shown in Fig. 7. The change in the slope of  $\sigma$  vs  $1/T$  curves of  $\text{Li}_{7.1}\text{Ta}_{0.9}\text{Zr}_{0.1}\text{O}_6$  corresponds most likely again to the transition from extrinsic to intrinsic mechanism of conductivity. The activation energies are  $0.50\text{ eV}$  and  $0.60\text{ eV}$  in the lower and higher temperature regions respectively. A similar change in the slope of the  $\sigma$  vs  $1/T$  plot of  $\text{Li}_{7.3}\text{Ta}_{0.7}\text{Zr}_{0.3}\text{O}_6$  is observed at a higher temperature, suggesting that the increased conductivity observed in the  $\text{Li}_{7+x}\text{Ta}_{1-x}\text{Zr}_x\text{O}_6$  phases is due to the larger concentration of mobile  $\text{Li}^+$  ions.  $\text{Li}_{7.4}\text{Ta}_{0.6}\text{Zr}_{0.4}\text{O}_6$  is in the region of extrinsic conductivity for the entire range of temperature measured.

In Table 1, we summarize conductivity data for the best Li solid electrolytes. It may be concluded that solid solutions of lithium hexaoxometallates are also members of good lithium ion conducting solid electrolytes.

Fig. 7

The temperature dependence of conductivity of  $\text{Li}_{7+x}\text{Ta}_{1-x}\text{Zr}_x\text{O}_6$  phases

Table 1 Conductivity data for Li compounds.

Compounds	$\sigma_{RT}$ ( $\Omega\text{cm}$ ) <sup>-1</sup>	$\sigma_{200}$ ( $\Omega\text{cm}$ ) <sup>-1</sup>	Activation Energy (eV)	Temp. Range (°C)	Ref.
Li- $\beta$ -Al <sub>2</sub> O <sub>3</sub>	$1.3 \times 10^{-4}$	$2.0 \times 10^{-3}$	0.19 0.36	-100 - 180 180 - 800	8
Li <sub>14</sub> Zn(GeO <sub>4</sub> ) <sub>4</sub> (LISICON)		$1.7 \times 10^{-4}$	0.50	50 - 300	9
Li <sub>4</sub> B <sub>7</sub> O <sub>12</sub> Cl <sub>0.68</sub> Br <sub>0.32</sub>	$5.4 \times 10^{-7*}$	$6.5 \times 10^{-4}$	0.53	50 - 230	1
Li <sub>3.75</sub> Si <sub>0.75</sub> P <sub>0.25</sub> O <sub>4</sub>	$4.8 \times 10^{-7*}$	$1.0 \times 10^{-3}$	0.60	30 - 230	1
Li <sub>4.4</sub> Si <sub>0.6</sub> Al <sub>0.4</sub> O <sub>4</sub>	$2.8 \times 10^{-7*}$	$7.6 \times 10^{-4}$	0.58	70 - 230	1
Li <sub>4.6</sub> Al <sub>0.6</sub> Si <sub>0.4</sub> O <sub>4</sub>		$7.7 \times 10^{-5}$	0.68	85 - 230	1
Li <sub>7</sub> Ta <sub>0.7</sub> Nb <sub>0.3</sub> O <sub>6</sub>	$7.3 \times 10^{-8*}$	$4.3 \times 10^{-4}$	0.63	80 - 230	this work
Li <sub>7</sub> Ta <sub>0.6</sub> Bi <sub>0.4</sub> O <sub>6</sub>	$7.3 \times 10^{-8*}$	$3.0 \times 10^{-4}$	0.60	50 - 230	this work
Li <sub>7.4</sub> Ta <sub>0.6</sub> Zr <sub>0.4</sub> O <sub>6</sub>	$3.4 \times 10^{-7*}$	$4.0 \times 10^{-4}$	0.52	50 - 230	this work

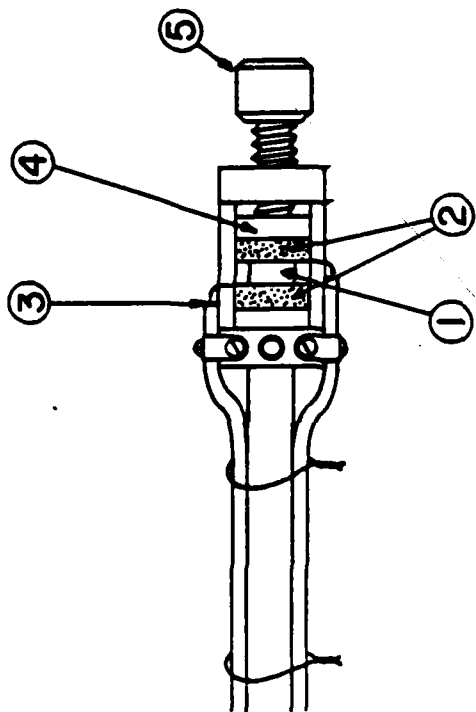
\* extrapolated value

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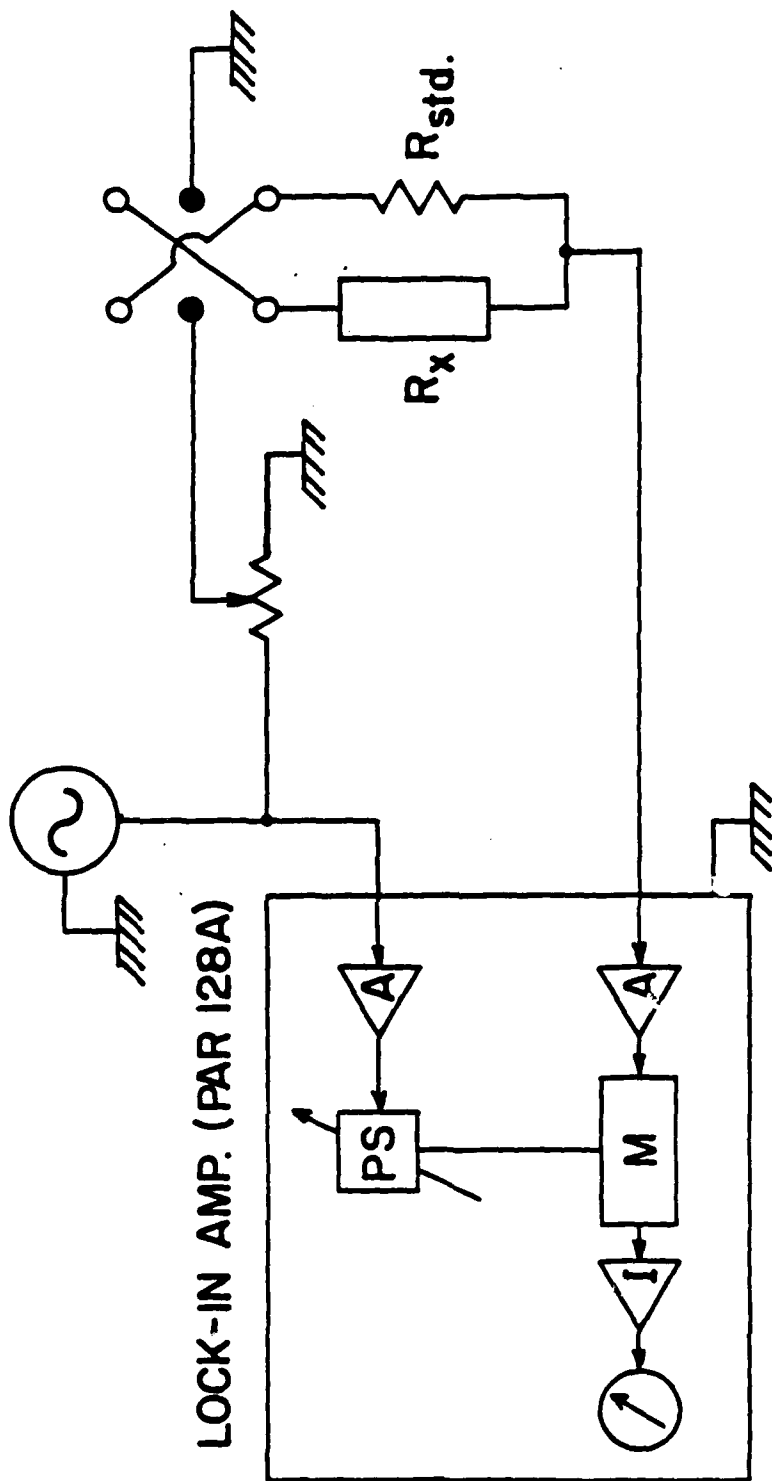
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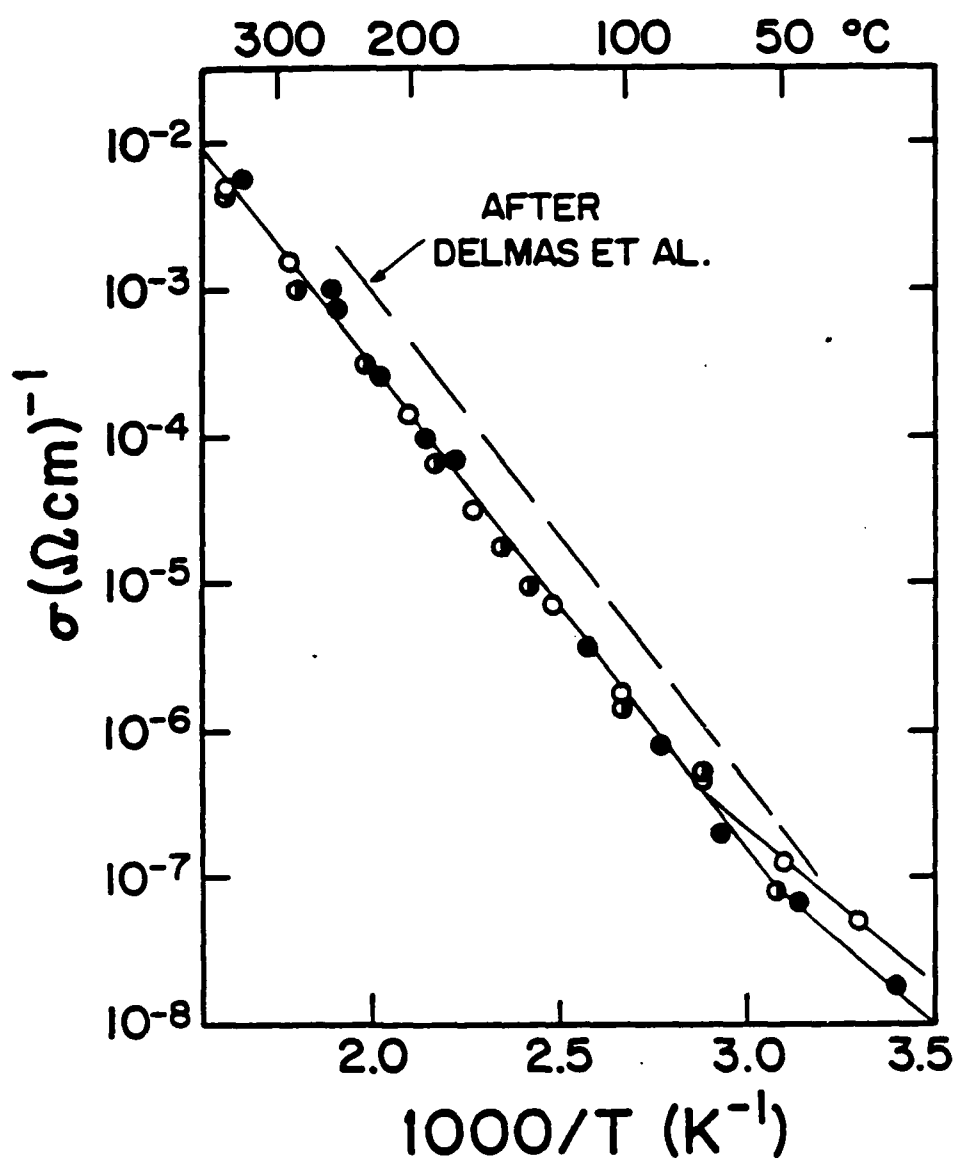


FIG. 3

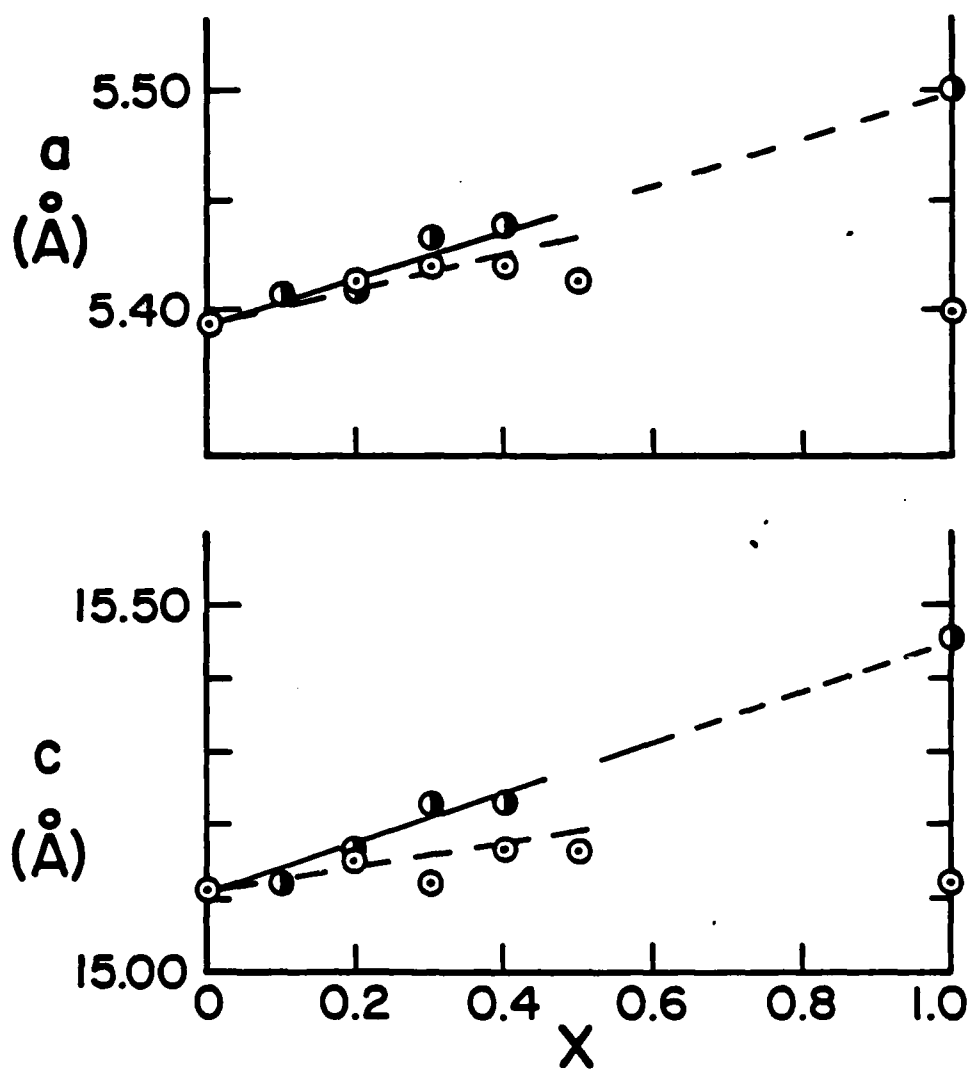


FIG. 4

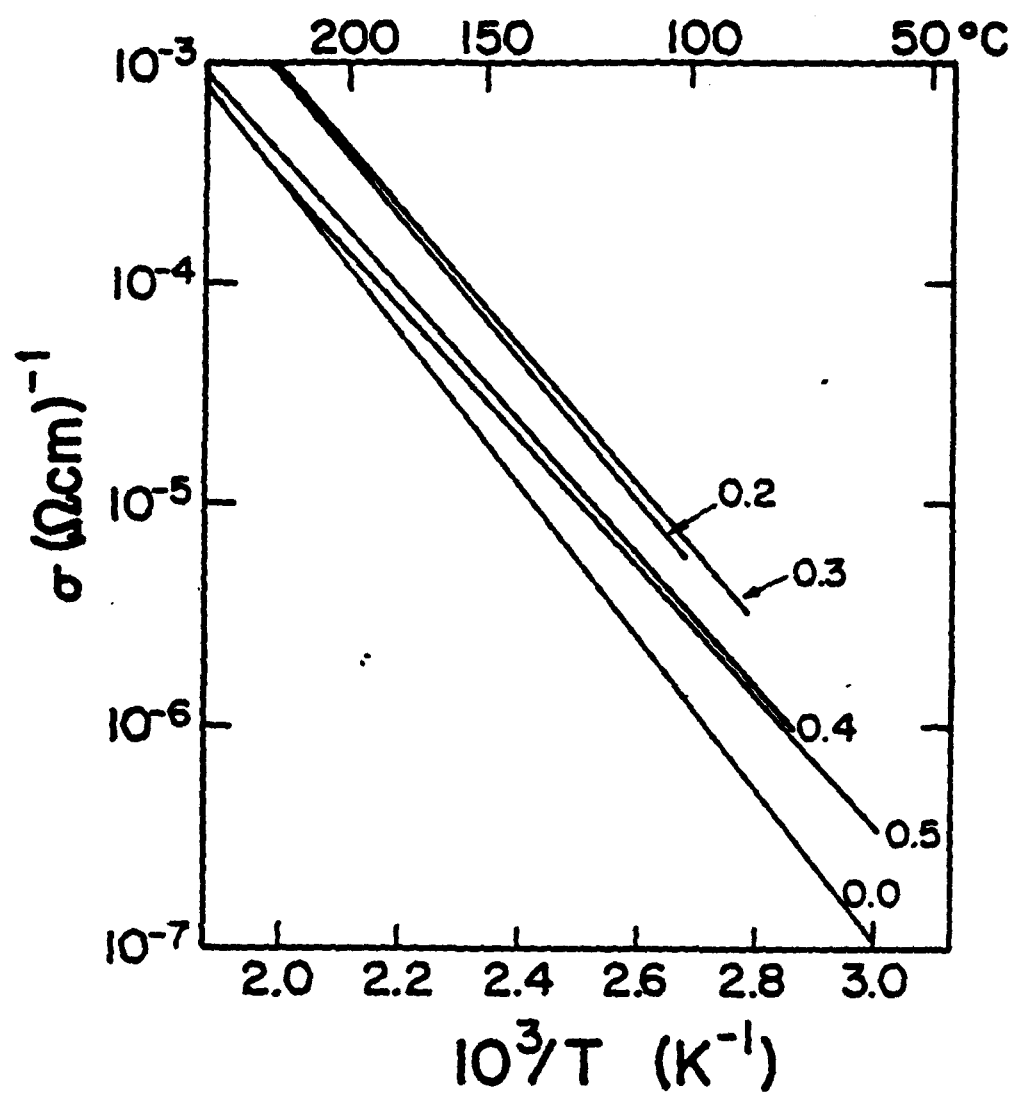


FIG. 5

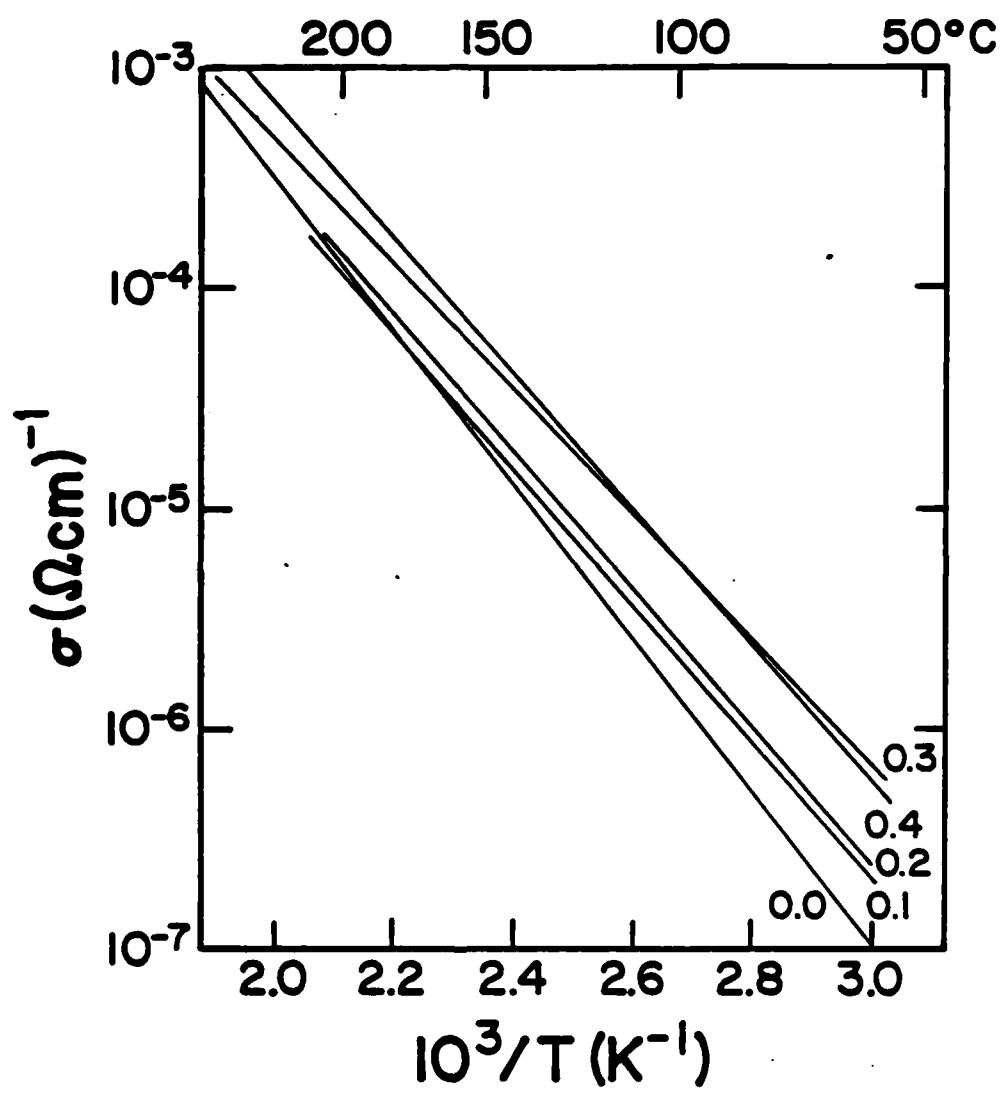


FIG 6

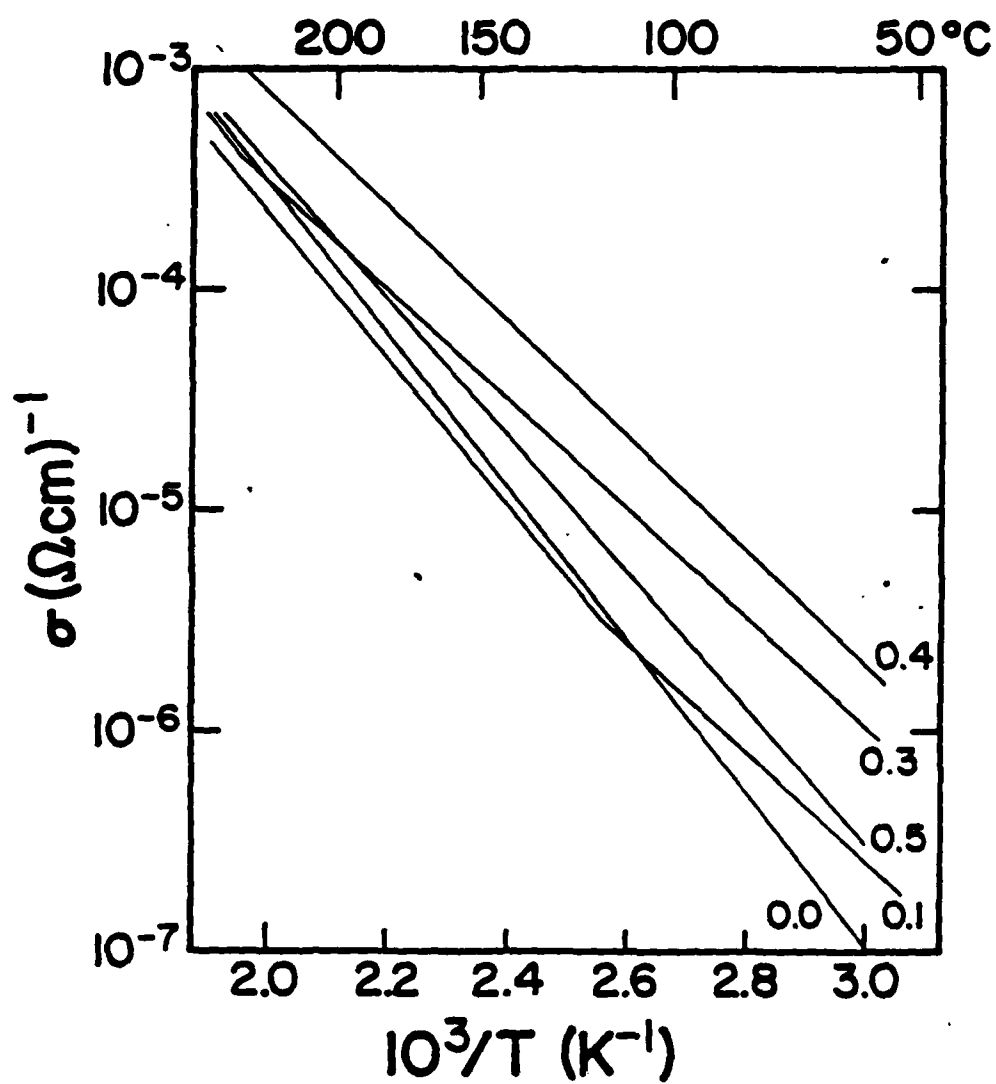


FIG. 7

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